

EVALUATION OF A CONDUCTIVE POLYMER-BASED SENSOR FOR DETECTION OF HYDRAZINES AT THE PART-PER-BILLION LEVEL*

Dan Curran
I-NET Space Services
Kennedy Space Center, FL

Mitch Zakin
Spectral Sciences, Inc.
Burlington, MA

Dale Lueck
National Aeronautics And Space Administration
Kennedy Space Center, FL

ABSTRACT

A conductive polymer-based hydrazine sensor (CPHS) was developed by Spectral Sciences, Inc., and Spire Corp. under an Small Business Innovative Research (SBIR) contract for the United States Air Force (USAF). During preliminary testing, the sensor showed promise as a dosimeter with the ability to detect hydrazine (N_2H_4) and unsymmetrical dimethylhydrazine (UDMH) at levels well below the proposed threshold limit value (TLV) of 10 part per billion (ppb). The original sensor developed and tested by Spectral Sciences and Spire Corp. demonstrated a minimum detectable dose of approximately 1 part per billion-hour (ppb-hr) and a saturation dose of approximately 250 ppb-hr in dry conditions, offering adequate coverage of the proposed TLV limit of 80 ppb-hr (8 hours at the proposed TLV level of 10 ppb). However, initial testing in a more realistic humidified environment [relative humidities (RH) to over 60 percent] indicated an increased sensor reactivity, yielding a saturation dose of only approximately 30 ppb-hr at humidities greater than 60 percent. A second version of the sensor (CPHS2) was fabricated utilizing a thicker polymer film in an attempt to increase the saturation dose back up to a level that would provide a better dynamic range. Initial tests of the CPHS2 by Spectral Sciences at the NASA Toxic Vapor Detection Laboratory (TVDL) in November 1993 exhibited a minimum detectable dose in the range of 1 to 2 ppb-hr, an increase in the saturation dose to approximately 150 ppb-hr in humid conditions and a measurement accuracy of ± 20 percent.

The CPHS2 sensors are currently undergoing tests at the TVDL. The TVDL has the unique ability to generate calibrated sample vapor streams of N_2H_4 and UDMH over a range from less than 10 ppb to thousands of parts per million (ppm) with full environmental control of humidity (0 to 90 percent) and temperature (0 to 50 °C). The polymer-based sensors will be subjected to extensive testing over a wide range of humidities at N_2H_4 and UDMH concentrations of 12.7 and 10.6 ppb respectively.

INTRODUCTION

This report presents the results obtained during tests performed on a conductive polymer-based hydrazine sensor at the NASA Toxic Vapor Detection Laboratory (TVDL) located at Kennedy Space Center, Florida. The testing was conducted at the request of the USAF, Space and Missile Systems Center to provide additional data on the response of a sensitive hydrazine selective sensor developed by Spire Corp. with Spectral Sciences under a Phase II SBIR program.

Preliminary development showed that films of the polymer poly(3-hexylthiophene) (P3HT), when doped with nitrosonium hexafluorophosphate (NOPF₆) become conductive and extremely sensitive to hydrazines. Early testing of sensors fabricated with 1500 angstrom (Å) thick films of the polymer/dopant material and monitored for resistance showed a significant and irreversible increase in resistance when exposed to constant low (ppb) levels of hydrazines.

*This work was performed under contract no. NAS10-11943 with NASA, John F. Kennedy Space Center, Florida.
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The resistance increase was proportional to the dose by a logarithmic function. In the most nearly linear portion of the graph of natural log of normalized resistance ($\ln(R/R_0)$) versus dose (ppb-hr) the response approximates a first order system (Figure 1) if the dose rate is held constant.

$$\ln(R/R_0) = k d \quad (1)$$

where d is dose and k is a proportionality constant.

Example of Sensor Response to Constant Hydrazine Exposure

Exposure Conditions: 12.7 ppb N₂H₄ at 40% R/H, and 25°C

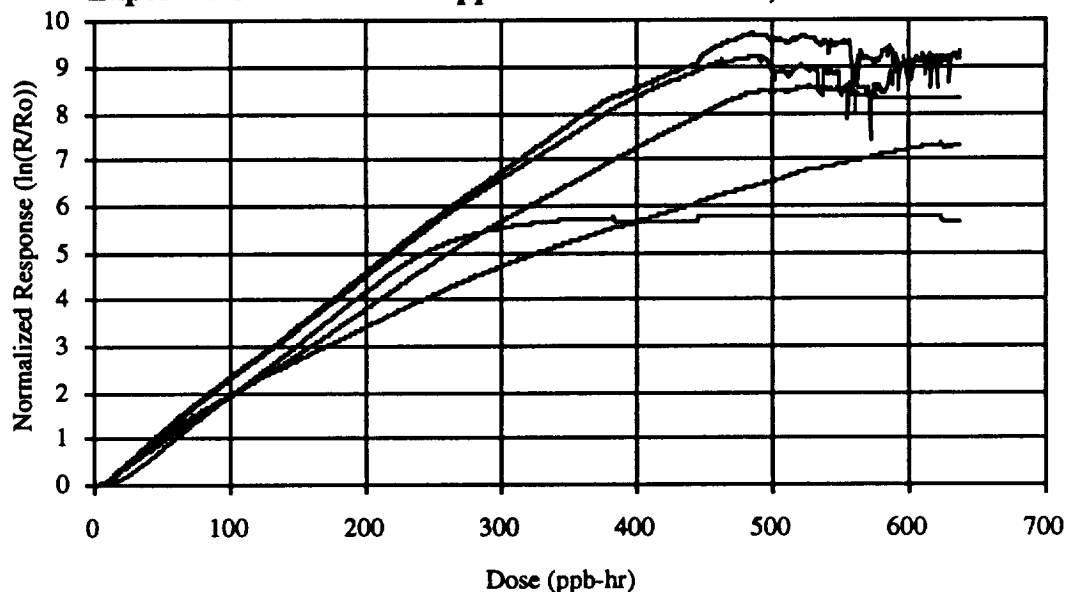


Figure 1. Normalized sensor response through entire dynamic range for different sensor units

When exposed to dry hydrazine vapor samples, these original sensors showed a minimum detectable dose of approximately 1 ppb-hr and a saturation dose of approximately 250 ppb-hr. The sensitivity of the sensor increased in humidified vapor samples greater than 25 percent relative humidity, decreasing the saturation dose of the sensors to approximately 30 ppb-hr. In order for the sensor to be useful as a hydrazine/UDMH personal dosimeter, which is the ultimate goal of this project, the dynamic range had to be expanded in environmental conditions comparable to potential field conditions.

The results of the developmental work done by Spectral Sciences Inc. on the P3HT/NOPF₆ system determined that by increasing the thickness of the polymer film, the dynamic range of the sensor could be expanded to meet the proposed TLV dose of 80 ppb-hr. Another version of the sensor was fabricated with a film thickness of 6000 Å. The amount of dopant applied to the sensor was also increased. These modified sensors underwent limited testing by Spectral Sciences to confirm an increase in the saturation dose to approximately 150 ppb-hr when exposed to humidified UDMH vapor in air.

The TVDL was tasked with further characterizing the response of these thicker film sensors. The requested testing included exposure to nominal 10 ppb vapor streams of UDMH and N₂H₄ at a range of relative humidities from 0 percent to 60 percent.

APPARATUS

SENSORS

The sensors provided by Spire Corp. were fabricated in December 1992. They consist of a substrate of quartz 1.0 inch long by 0.5 inch wide by 0.02 inch thick, on which a 1000 Å-thick layer of gold (Au) is plated, forming the electrical contacts for resistance measurements (Figure 2). At the center of the sensor a 0.25 inch square area consists of 40 pairs of interdigitated Au fingers. The fingers are 20 μm wide and spaced 20 μm apart. Over the interdigitated electrodes, a thin film of P3HT is deposited using a spin coating technique. The resulting film is approximately 1 cm. square with a thickness of 6000 Å ±250 Å. The polymer is virtually nonconductive until it is doped by dipping the individual sensors into a solution of NOPF₆ until an initial resistance of 5 to 50 kΩ is achieved. The film deposition and doping procedures are done in a glove box under a flow of dry nitrogen. The sensors are then stored individually in nitrogen blanketed vials at a temperature of -40 °C.

In order to eliminate sensitivity to humidity, each sensor was conditioned in humidified instrument grade laboratory air before any exposure test was initiated. During this conditioning process, the resistance of the polymer increases slightly then begins to oscillate around some average value. This conditioning period generally requires 24 to 48 hours of exposure.

Conductive Polymer-based Hydrazine Sensor

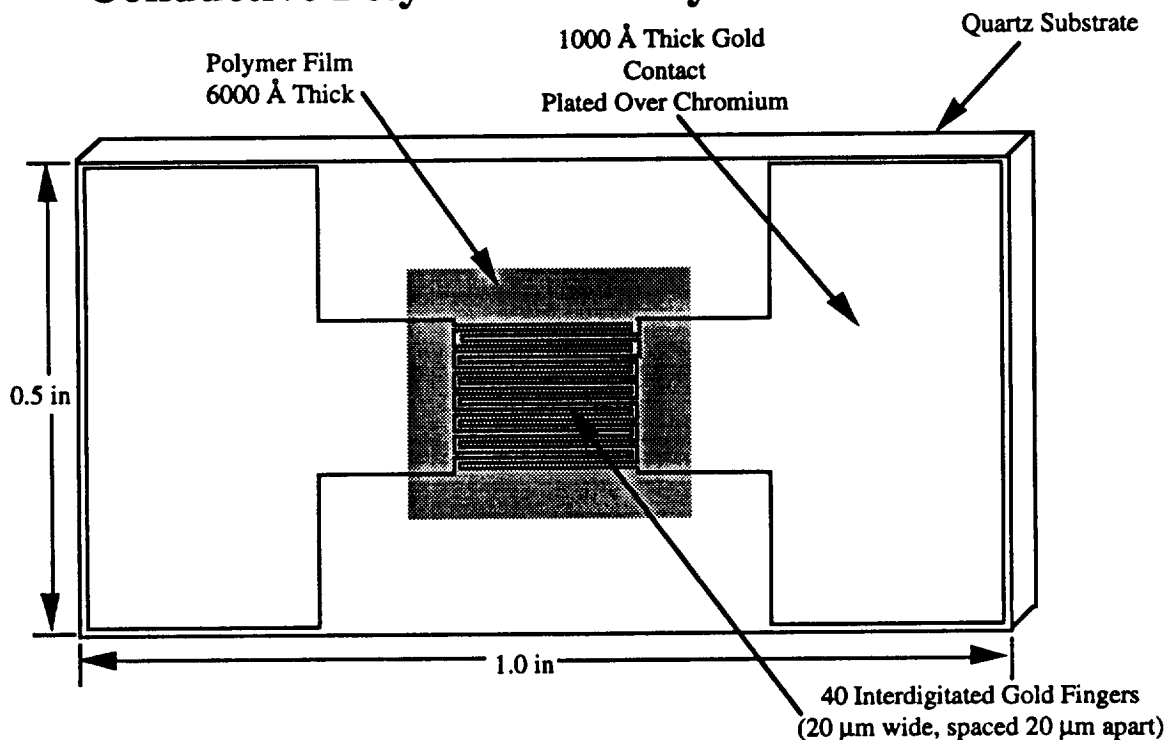


Figure 2. Conductive Polymer Hydrazine Sensor, as supplied for testing by Spire Corp.

TEST VAPOR GENERATION

The TVDL test apparatus (Figure 3) was designed to deliver known concentrations of N₂H₄ and UDMH at controlled conditions of temperature and relative humidity. The Kin Tek Span Pac (Model 361) is a precision standard toxic vapor generator that produces controlled concentrations. The vapors are further diluted by controlled mixing with humidified instrument grade air from a Miller Nelson Model HCS-301 flow/temperature/relative humidity (F/T/RH) controller. Each vapor generator consists of three permeation devices in three individually

SENSOR TEST CONFIGURATION

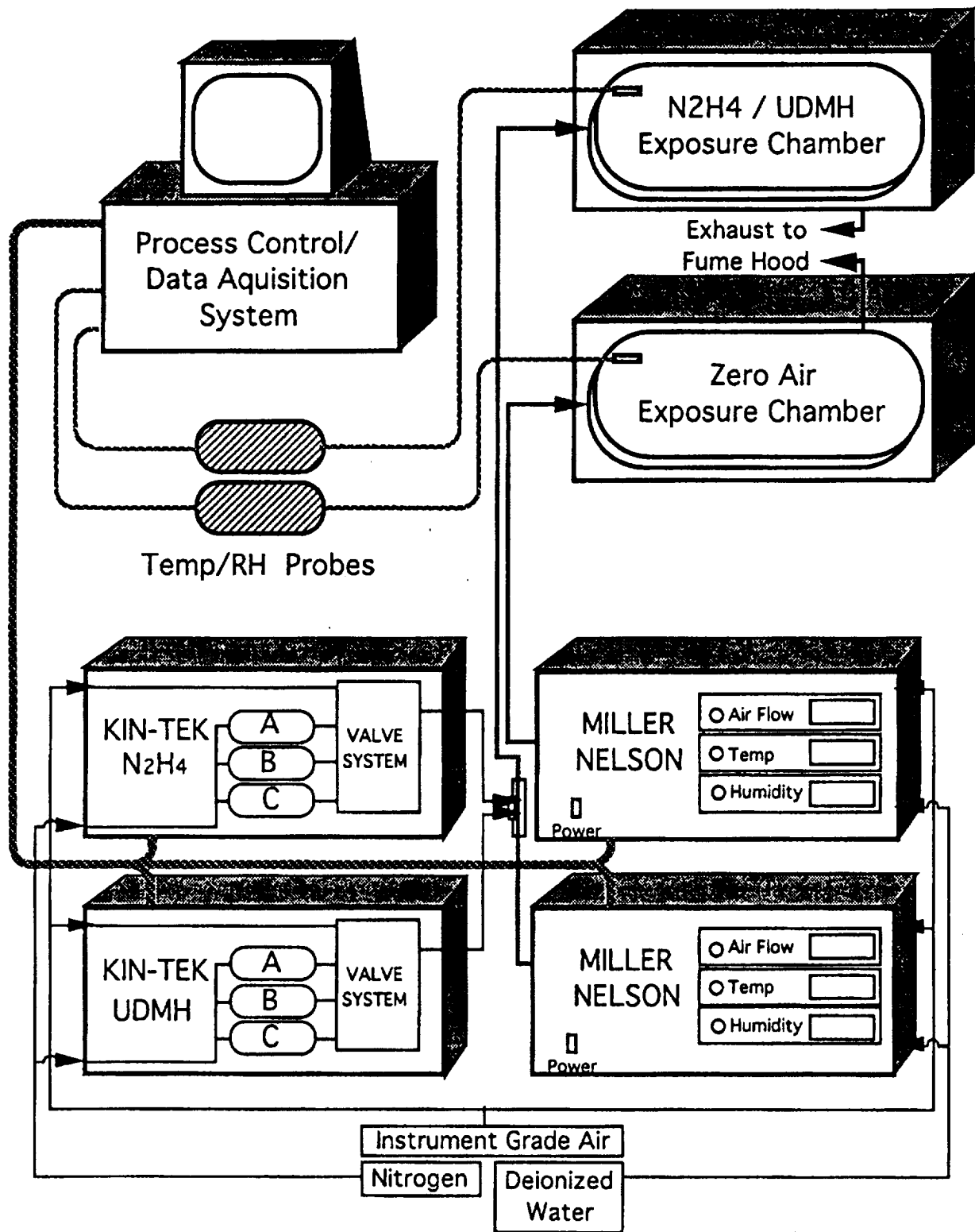


Figure 3. Diagram of laboratory test setup

temperature-controlled ovens. For UDMH, stainless steel permeation devices were used and, for N₂H₄, glass permeation devices were used. Two vapor generators were used to provide concentrations of UDMH and N₂H₄ vapors for these tests.

The F/T/RH controller and a computer Process Control and Data Acquisition System (PCDAS) were used to precisely control the flow, temperature, and RH of the diluent air. This provided the desired vapor concentrations with a range of temperature and RH conditions. Two F/T/RH controllers were used for the test, one for providing diluent air to the exposure vessel and the second for providing hydrazine-free "zero" air for conditioning and recovery. Upstream of the exposure vessel, a specially designed Teflon injection tee was used to inject the N₂H₄ or UDMH vapor from the vapor generator to be mixed with the conditioned diluent air from the F/T/RH controller. The injection tee was designed to optimize vapor delivery and mixing efficiency. Vaisala temperature/humidity sensors (Model HMP 130Y Series) were used for monitoring the temperature and humidity in the N₂H₄/UDMH and zero-air exposure chambers.

Two exposure chambers were utilized for sensor testing. Both consisted of polyethylene zip lock bags large enough to allow multiple sensors, attached to a scanner card, to be placed in the chamber. The openings of the bags were closed enough that the purge of sample vapor produced pillow-shaped chambers. The bags were enclosed in an outer insulated box to eliminate the influence of ambient laboratory temperature fluctuations. One chamber was maintained as a hydrazine-free zero-air chamber, and the other as an N₂H₄/UDMH exposure chamber. Temperature/humidity sensors in each chamber actuated the PCDAS to adjust the output of the Miller Nelson F/T/RH controller as required to continuously maintain a constant temperature and humidity condition in each chamber.

SENSOR MONITORING SYSTEM

The sensor monitoring system hardware assembly and software package were also provided by Spire Corp. and Spectral Science Inc., set up during the SBIR phase of the sensor development. The following equipment was used during these tests:

- ZEOS 386-20 PC with Spire Corp. provided custom software
- Two Keithley model 617 programmable electrometers, one programmed as a voltmeter, and one as an ammeter
- One Keithley model 220 programmable current source
- One Keithley model 705 programmable scanner with a 7056 internal card
- Four cables connecting all Keithley instruments to the computer in parallel
- Four triaxial cables and a shielded multiplexer box
- One Keithley model 7067 four-wire scanner card with 10 channels

The software package along with the above hardware allows resistance monitoring of up to 10 sensors at one time when attached to the scanner card. During exposure to N₂H₄ and UDMH, the resistance of the sensors can increase from 1 k Ω to 100 M Ω . The electronics system was designed to precisely measure the resistance of the films over this wide range by applying a minimum of current (0.1 μ A) to the sensors. Low-current resistance measurements are critical in order to avoid heating the films, which can cause resistance to increase.

TESTING AND RESULTS

TESTS PARAMETERS

The test plan for the humidity characterization of the conductive polymer-based hydrazine sensors was generated by the USAF and Aerospace Corp. based on sensor development work done in the SBIR phase of the program. The test plan required exposure of a set of sensors to constant nominal 10 ppb vapor concentrations of N₂H₄ and UDMH at specified values of relative humidities (0 percent, 20 percent, 40 percent, and 60 percent RH). During the humidity testing the only condition that varied was relative humidity levels of hydrazine vapor samples. One set of sensors was exposed to each humidity level. Two sets of sensors were tested in N₂H₄ at 60 percent RH because the response of the first set tested at 60 percent RH did not seem to correlate with the other test sets.

The actual concentrations of N₂H₄ and UDMH were 12.7 ppb and 10.6 ppb, respectively. Test vapor

concentrations were verified by impingement scrubbing and coulometric titration. For each condition, a group of five sensors, chosen at random from the lot of 100 sensors provided, were exposed simultaneously to determine response scatter. Prior to each test, excluding the exposure tests done in 0 percent RH conditions, the sensor set was conditioned in the zero-air chamber at a controlled 50 percent RH and 24 °C for a period of 24 to 48 hours in order to eliminate sensor response to H₂O. The sensors exposed to dry N₂H₄ and UDMH were conditioned in zero-air at 0 percent RH for the same time period.

Before the sensors were placed in the hydrazine exposure chamber, the chamber and scanner card surfaces were given ample time to equilibrate and passivate to ensure a stable N₂H₄/UDMH vapor concentration. Sensor sets were typically exposed to a minimum dose of 200 ppb-hr, although several sets were exposed until saturation was reached in order to determine a representative dynamic range. During each test, the sensor set was monitored continuously using the supplied sensor monitoring system. Resistance measurements were taken at 5-minute intervals throughout the exposure period.

RESULTS AND DISCUSSION

On the basis of earlier testing conducted on this type sensor by Spire Corp. and Spectral Sciences, the characteristic selected to compare sensor-to-sensor and test-to-test response was the k constant derived from Equation 1, $(\ln(R/R_0)=k \cdot d)$. K values were calculated for each sensor for every measurement. These k values were then averaged over the linear range of sensor response (dose range of 0 to 150 ppb-hr). The linear range also corresponds to the range of concern pending the proposed ACGIH lowering of the allowable TLV to 10 ppb for all hydrazines. Figures 4 and 5 graphically display the change in k over the range of humidities tested. A summary of average k values and standard deviations of each sensor set are shown in Table 1. Note that each row in Table 1 represents a different set of 5 sensors, because resistance changes in exposed sensors are irreversible.

When reviewing the humidity test results, it can be noted that the five-sensor average k value seems to remain consistent in humidities from 20 percent to 60 percent. The sensitivity of the sensors to UDMH decreased when compared to the tests done by Spire at the TVDL in November 1992, using the same test method. Prior tests by Spire Corp. done in UDMH at 40 percent RH showed k values of $.035 \text{ (ppb-hr)}^{-1}$, while the average k values for sensors exposed to UDMH at 40 percent RH in the tests described in this report is $.017 \text{ (ppb-hr)}^{-1}$. The minimum detectable dose, calculated from a readily measured 10 percent change in resistance, is approximately 7 ppb-hr and the saturation dose was about 250 ppb-hr. A possible reason for the loss of sensitivity in the TVDL tests could be that at the time these most recent tests were conducted, the sensors had been in storage for over 1 year.

Table 1. Average k values for 12.7 ppb N₂H₄ and 10.6 ppb UDMH continuous exposure humidity tests

N ₂ H ₄ Humidity Exposure k Values*			UDMH Humidity Exposure k Values*		
Percent Relative Humidity	5-Sensor Average k Value	Standard Deviation	Percent Relative Humidity	5-Sensor Average k Value	Standard Deviation
0	0.01650	0.00234	0	0.00951	0.00343
20	0.01625	0.00427	20	0.01937	0.00257
40	0.01883	0.00172	40	0.01743	0.00241
60 (Run 1)	0.02558	0.00418	60	0.01807	0.00712
60 (Run 2)	0.02197	0.00683			

*Units = (ppb-hr)^{-1}

Although the exact resistances of the individual sensors as verified at the time of fabrication was not available, the resistances measured at the time of testing were all within the acceptable range of 5 to 50 k Ω described in the fabrication procedure.

UDMH Humidity Test Results

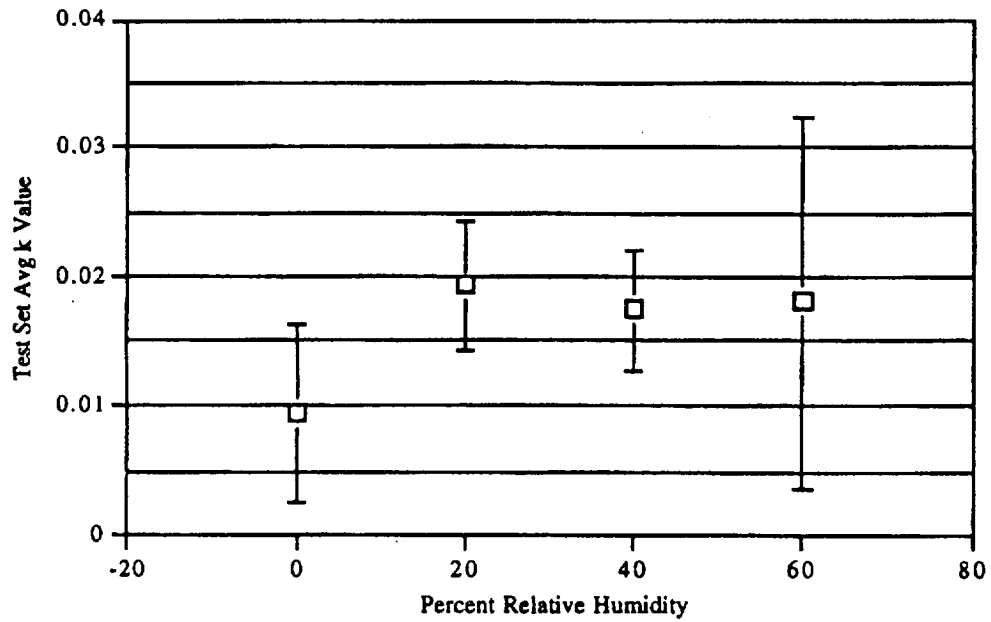


Figure 4. Average k values from UDMH relative humidity tests (error bars represent \pm two standard deviations)

N₂H₄ Humidity Test Results

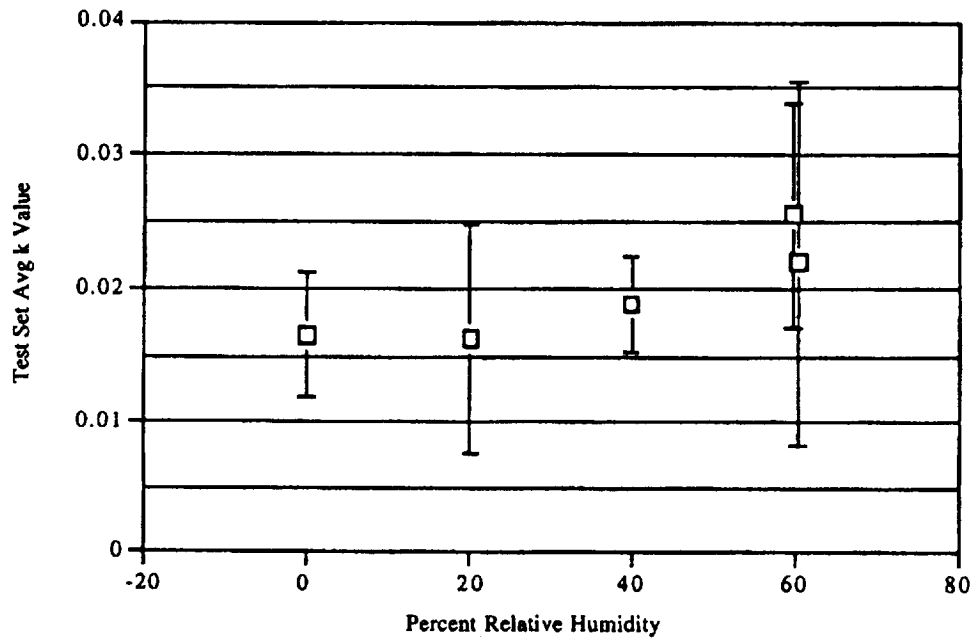


Figure 5. Average k values from N₂H₄ relative humidity tests (error bars represent \pm two standard deviations)

The main area of concern with these results is that the scatter in some of the sample sets is significantly larger than the ± 20 percent reported in previous tests performed on this version of the sensor. This increased scatter may also be a function of the long storage period or may possibly be related to the small lot fabrication techniques. A better controlled application of the polymer film and a more homogenous distribution of the dopant within the polymer would likely produce sensors with more consistent film thicknesses, tighter initial resistance ranges, and more consistent k values. Also the quartz/Au substrates had been coated and stripped several times, leading possibly to damage to the Au electrodes, resulting in further dissimilarity.

CONCLUSIONS

The first set of tests in humidified hydrazine vapors confirmed results of earlier limited testing showing minimal effect of humidities from 20 to 60 percent on average sensor response to constant 10 ppb vapor concentrations of hydrazine and UDMH in air. Sensors showed an easily measurable lower limit of response of approximately 7 ppb-hr and a saturation dose of approximately 250 ppb-hr. The fact that the sensors had been in storage for over one year at the time these tests were performed speaks well for the stability of the polymer/dopant system. The age of the sensors and its possible influence on results in this report should not be overlooked. Only further testing on fresh sensors will verify age effects. Repeatability between sensors is still a matter of concern, although several corrective measures might improve scatter, such as, better control of film thickness deposited, concentration and distribution of dopant in the film, and electrode configuration.